Continuous flow-microwave reactor: Where are we?

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A B S T R A C T

This article presents the different microwave continuous reactors existing, which are reported in literature to carry out chemical synthesis with a more efficient way. It shows how the methods and tools of chemical engineering can be useful and necessary to define, characterize and optimize the microwave reactors. This review scans continuous microwave reactors, by describing the different types of microwave technologies used (multimode, single-mode, coaxial or guided transmission . . .). It then focuses on the various existing reactor geometries and on the control of the electromagnetic field homogeneity. The problem of temperature measurement and overall instrumentation is also addressed (input power, reflected power, continuous adaptation . . .).

This review scans the most efficient microwave continuous flow reactors existing in the literature and highlights how the microwave technology is used as well as chemical engineering tools. It points out the reactors geometries, the control of the electromagnetic field and the measurement of the physical parameters (Temperature, microwave power, etc.).

Finally, the scale-up of continuous-flow microwave reactors is examined through the existing lab-scale and semi industrial pilot plants described in literature.

1. Introduction: towards continuous flow process

Since the application of microwaves to chemistry launched by Gedye [1] and Guiguere [2] in 1986, many researchers studied the effects of microwave heating on numerous chemical reactions in batch systems. The number of articles published is very impressive: more than 43,750 publications on MW-assisted reactions between 1986 and 2016! (Source Thomson Reuters, based on Scopus, keywords search on 'microwave and reaction'). The enthusiasm of the scientists for the microwave systems remains always strong especially in organic synthesis, extraction, polymer, biomass area. (respectively, 19,700; 15,500; 10,800; 1050 publications).

The main benefits obtained in chemistry consist in an increase the reaction rate, the reduction of the side-products, the improvement of the product purity compared to conventional heating. Chemistry under microwave enables the reduction of the solvent quantity, the use of green solvents as water and sometimes synthesis under dry media conditions can be carried out. These advantages have been listed by many authors [3–5] and microwave processes are known now as environmentally friendly process and which enables energy saving.

The major limit of microwaves is the penetration depth which is only a few centimetres in usual solvents and chemical environments with favourable properties that excludes the use of high-volume reactors.

Coupling microwave heating and continuous flow technology eliminates the main drawbacks of microwaves and creates a very promising way to produce high value added chemicals or key pharmaceutical intermediates since unlike the batch, the continuous flow has been demonstrated to facilitate process intensification and contribute to a safe, efficient and sustainable production [1,4].

The first systems coupling microwave and continuous flow were studied in the 1980's and concerned the polymer heating and the solid drying [6,7]. In chemical synthesis, about 780 papers on the continuous reactors have been published since 30 years, 286 are in the field of microwave flow chemistry and 220 deals with microwave continuous reactor which described systems with a large range of size from some millimetres or less to some centimetres. The continuous flow under microwaves appears in 1990's at the same time than flow chemistry. The reactor consisted

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in a Teflon coil placed in a commercial microwave oven. It has been used for several organic syntheses, including preparative-scale samples, but the quantities remain small because of the limited volume of the reactor (10 mL°).

In most papers published, the emphasis is on the chemical reactions and the part dedicated to the reactor consists generally in a brief description of the systems. Among the 43,750 articles, only 430 are identified in the area of chemical engineering that represents less than 1% of the papers! The percentage falls dramatically to 0,2% when using the key-words microwave; chemical reaction and chemical engineering.

The main objective of this work is to present a state of the art in the area of the continuous microwave systems, to provide a critical analysis, to highlight the process parameters and to propose some tools of chemical engineering useful for the development of more efficient microwave processes.

2. About energy and heating

Light that interacts with matter can be reflected, absorbed or transmitted, wherever absorption occurs, heat energy is generated. As light, microwaves are electromagnetic radiations (EMR), which are synchronized oscillations of the electric and magnetic fields propagating at the speed of light through a vacuum. The oscillations of the two fields are perpendicular to each other and perpendicular to the direction of energy and wave propagation, forming a transverse wave.

The energy of the wave is stored in the electric and magnetic fields. In the quantum theory of electromagnetism, electromagnetic microwave radiations consist of photons, the elementary particles responsible for all electromagnetic interactions.

The quantum energy of microwave photons is in the range 0.000001 to 0.001 eV (300 MHz to 300 GHz) which is in the range of energies separating the quantum states of molecular rotation and torsion. Since the quantum energies are a million times lower than those of X-rays, they cannot produce ionization and the characteristic types of radiation damage associated with ionizing radiation. They also cannot play a role in chemical bonding where quantum energy is at least a thousand times bigger.

Microwave heating is based on the electromagnetic energy conversion which requires the existence of a direct interaction between the bulk and the microwaves and a sufficient penetration depth. For a given frequency, this interaction exists only if the dielectric properties of the bulk are suitable. The latter are very sensitive to any change in composition or in temperature. The energy conversion can be due to several mechanisms such as dipolar polarization, ionic conduction, Wagner effect . . . In the case of dielectric system heating, dipolar polarization and ionic conduction are the most frequently encountered phenomena. Even without chemical reaction, the specificity of microwave heating, results from the temperature dependence of dielectric properties (Fig. 1). In many cases, the complex dielectric permittivity depends on the temperature and the dynamic behaviour of microwave heating is then governed by this thermal change [8].

It is important to specify that for continuous flow applications, the dielectric and thermal properties, in the reaction volume are both spatially and temporally variable. For example, Fig. 2 shows the behaviour of dielectric properties during the reaction of decomposition in isothermal mode (89 °C) of AIBN [2,2′-Azobis(2-methylproprionitrile)] in TMSN [Tetramethylsuccinonitrile] (Scheme 1) [9].

On top of that variability of the properties is not the only key factor, for a good coupling of the electromagnetic field with the medium. The value itself of the dielectric properties is important, since the electric field propagation and amplitude depend respectively on the real and imaginary part of the dielectric

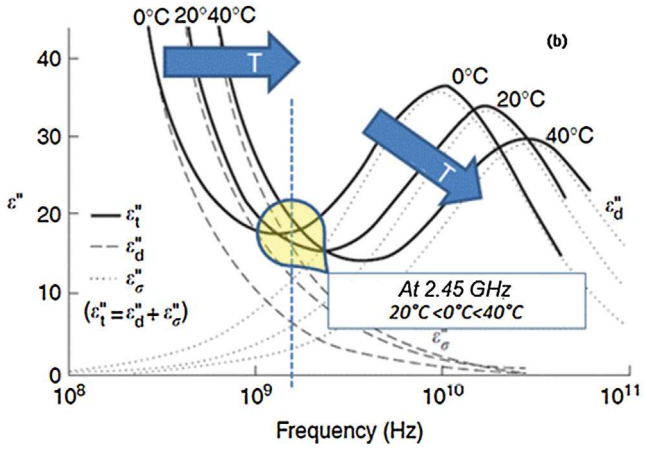


Fig. 1. Frequency and temperature dependence of dielectric properties of NaX zeolites [8].

permittivity. For example, the higher the real part of the dielectric permittivity is, the more important reflexions are. For liquid medium with a priori favourable properties, like water or ionic solvents, when the imaginary part is propitious for heating, important reflexions can dramatically decrease the electromagnetic field intensity and thereby the overall efficiency of the energy conversion. When dipolar polarization is the main phenomenon, dielectric heating involves unorganized movements at micro scale due to the inability of molecule clusters to move exactly with the electric field. This hysteresis phenomenon explains how the organised energy of electromagnetic field is transferred as Brownian movement into matter, many authors call this phenomenon **"**internal friction**"** [10]. The characteristic time scale of this conversion is some picoseconds [11], i.e. very fast compared to thermal diffusion which is around some seconds.

For those reasons, it is expected that a homogeneous electric field gives an isothermal medium, whereas for fast heating rates, classic thermal transfers need high thermal gradients at the system walls (Fig. 3). In fact, this absence of thermal boundary layer at the wall – sometimes called inversion of the thermal gradient compared with conventional heating (when the walls are colder than the bulk) – gives the ability to raise the heat source for fast homogeneous heating. At the opposite, inhomogeneous electromagnetic fields produce local high thermal gradients called **"**hot spots**"**.

Many surveys have shown that rapid heating and enhancements of chemical yields are achieved with microwaves [12–15]. In solid chemistry and in heterogeneous solid-liquid systems, many experiments led to significant differences in reaction rates obtained between conventional and microwave heating. If at least one of the components of a reaction mixture couples very strongly with microwaves, then it is possible to use that property to rapidly heat the reaction mixture and thereby obtain the final product more quickly and sometimes with a better yield. In the special case of heterogeneous reactions with solid phase or in general when dielectric properties increase with composition or temperature, the absorption rate of microwave energy also increases, hence thermal runaway can result; at the opposite when properties decrease the system is self-regulated. Consequently, controlling heating rate and electromagnetic field homogeneity are essential for both repeatability and industrial applications. Therefore, to achieve these objectives, one key step is the measurement of the dielectric properties and another is the modelling of the electromagnetic field.

For temperature and power control feedback, in a running process, one major problem results in the temperature

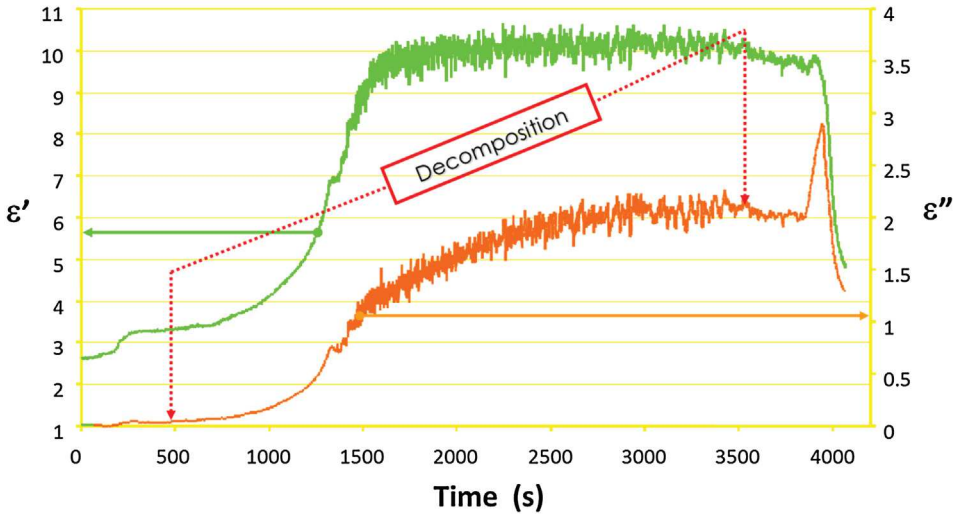
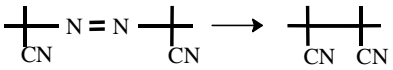


Fig. 2. Behaviour of electrical properties in isothermal mode at 89 °C [9].



Scheme 1. Thermal decomposition of AIBN.

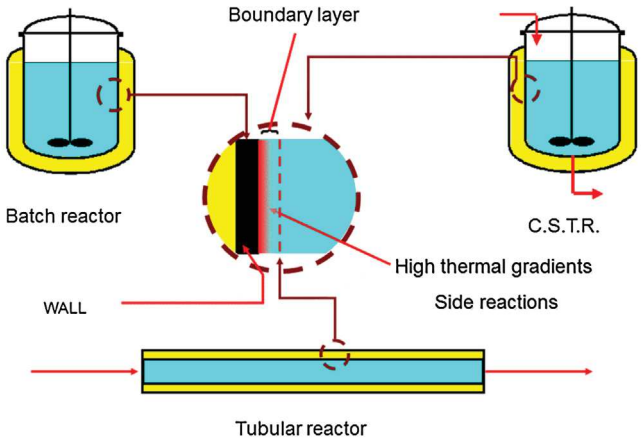


Fig. 3. Thermal boundary layer (conventional heating).

measurement, since direct measurement under microwave is rather delicate. The introduction of a metallic conductor in a cavity can interfere with the electromagnetic field and generate antenna effects. Thus, temperature measurement is very often carried out with fiber optic or IR sensors which respectively provide local and surface temperature. As discussed earlier, the heating of the reactor wall can be due to the thermal diffusion from the bulk or to a specific internal heat source depending on whether the reactor walls are transparent or not for microwaves. Thus in transient, IR sensors will give an inaccurate value of the bulk temperature. The temperature knowledge is the first step in a microwave heating study, since such a study involves solving Maxwell's equations of electromagnetism and the heat conduction equation, as told before, where all thermal, electric and magnetic properties of the material are non-linearly dependent on the temperature.

3. Microwave continuous flow systems: focus on the design of reactors

The easiest and most rapid way to build a continuous flow microwave reactor at the laboratory scale was to modify and to adapt some existing systems such as domestic ovens, multimode and single-mode microwave apparatus, firstly developed for a batch use. The results of these chemical synthesis carried out in such reactors have to be considered as demonstrative examples only; because of the non-control of the main parameters governing the microwave heating and the flow, the results are almost depending of the system used and the reproducibility becomes difficult and quite impossible.

The reactors were designed according to the chemical applications; in most cases, they consist in a simple tube implemented into the microwave cavity. The diameter and the length of the channel seem to be selected arbitrarily and the flow rate is chosen in order to obtain the right time residence in relation with the kinetics of the reaction. The hydrodynamics was not generally considered as a parameter which could influence the reaction rate.

Thus, the diameter of the channels – made generally in quartz or Teflon – could vary in the range of few hundred micrometres to some centimetres and the length between some centimetres to few dozen centimetres. In this last case, the channel consists generally in a coil to get a compact design and to facilitate its implementation into the microwave cavity. The reactor could be placed into multimode cavities as well as in single mode cavities operating at 2.45 GHz.

3.1. The continuous flow systems: a solution to scale-up microwave batch reactors

The development of continuous flow systems was first initiated with the aim to propose solutions to increase the quantity of production, to prove that scale-up of the process is possible and to demonstrate that the synthesis under microwave could be integrated to industry.

The first experiments were carried out into large pipe reactors (diameters more than a centimetre) simply introduced into commercial microwave ovens. Thus, the power of the microwave generator could reach 1.7 kW according the systems, the pressure

until 30 bar, temperature until 240 °C and the range of the flow rate from 1 L/h to 20 L/h.

To achieve heterogeneous as well as homogeneous reactions in a scale of dozen grams, a large microwave continuous-flow recycle reactor based on a modified Maxidigest 350 (Prolabo), using a 66 mL quartz glass cylinder reactor was specially designed for carrying out solid-liquid reactions [16]. The reaction mixture enters up flow from the bottom by a piston pump with variable flow rates between 30 and 335 mL/min for residence times of 12 s to 2 min. The system could operate in open or closed loop mode.

A continuous flow fixed bed reactor was inserted horizontally into a large microwave multimode oven [17]. The reactor, a Pyrex glass tube with 1.07 cm i.d and 39 cm length, was stuffed with the catalyst, a strongly acidic cation-exchange resin, and tested with two reactions (hydrolysis of sucrose, the homogeneous and heterogeneous esterification of benzoic acid with ethanol) at 140 °C and 7 bar with flow rate of 1 L/h [17,18].

Many flow reactors are commercially available to scale up in microwave process chemistry such as Milestone FlowSYNTH reactor which can operate under pressure (30 bar). It consists of a 200 mL PTFE tube placed vertically in a microwave multimode cavity (up to 1600 W). Moseley and co-workers [19–21] reported six homogeneous reactions investigated (Ortho Claisen Rearrangement, Naphthofuran Formation, Heck Reaction, Nucleophilic Aromatic Substitution Reaction) successfully carried out in this system with production rates between 1 and 6 L/h.

To scale up chemical synthesis to kilogram scale, a pilot plant microwave reactor was built by MLS GmbH (ETHOS PILOT 4000) [22]. The system consists in a vertical tubular reactor of 0.88 L (700 mm length) placed on a multimode microwave cavity equipped with four magnetrons that deliver a microwave power up to 200 W and two truncated pyramids mode stirrers. This system can operate with a pressure up to 60 bar and 240 °C with flow rates between 0.2–20 L/h [22,23]. Four IR sensors and two Ni-Cr/Ni thermocouples are used to record the temperature respectively along the tubular reactor and at the output of both the reactor and the cooler. The esterification of linalool was performed in this ETHOS PILOT 4000 at a 25 kg scale with 2.2 L/h flow rate [24].

An interesting apparatus was introduced by Morschhäuser et al. able to operate safely at high temperature/pressure (310 °C/60 bar) with a production on an industrial scale (up to 20 L/h) [25]. It consists in a cylindrical reactor (75 cm × 1 cm i.d) made of γ-Al_2O_3, transparent to microwaves inserted into a singlemode cylindrical waveguide. This reactor has been validated as a safe and energy efficient instrument using four chemical transformations with flow rates of 3.5–6.0 L/h.

Inserts (helical coil) made of PTFE impregnated with carbone C/PTFE were added into a glass tube continuous microwave reactor located into a microwave single mode unit (Biotage) to assist heating microwave low-absorbant solvants and to increase mixing [26]. A window in the microwave cavity permits the use of an IR camera to record the surface temperature of the reactor. Chemical reactions were conducted in low-microwave-absorbant solvants as the radical allylation of an iodolactone in carbon tetrachloride. A 78% yield was achieved (at 100 °C and 6 bar) however there was a temperature gradient from the center to the surface of the reactor (∼6–9 °C).

In order to increase the production to 1 kg/day, the concept of parallelization of reactors was followed. A multitubular milli-reactor/heat exchanger consisting of a cylindrical frame (1.2 cm i.d and 13.7 cm length) containing seven quartz tubes (166 mm length, 2 mm i.d) was developed. Fiber optic sensors were used to measure the temperature of the reaction mixture and the cooling liquid [27]. This system was tested successfully on the production of 1,3-diphenyl-2-propynyl piperidine catalyzed by Cu that has been deposited on the inner walls of the tubes. The energy uniformity in the tubular reactors was studied by measuring the microwave power absorbed by each tube filled with a specified solvent. This system was conceived following a previous study that highlighted the importance of the design of both the reactor and the microwave equipment to achieve a good performance [28].

3.2. Continuous flow systems: towards the reactor miniaturization

Coupling microwave heating and micro-reactors is a very promising approach from the point of view process intensification. Many systems have been developed since few years involving micro or milli-channels with diameters from some hundred micrometres to more currently some millimetres.

Generally, the running conditions require a flow rate range (110 mL/h) inferior than those used for channels with large diameter. The microwave power is also inferior (generally about 10–100 W max). In some of the proposed systems, pressure could reach 70 bar and temperature, 450 °C.

3.2.1. Narrow channels

In these following studies, the microreactors are genellary used as demontrative tools for chemical reactions under microwave irradiation. Because of the small channels diameter, they are limited to some milligrams of product.

In 2003, a glass micro-reactor (from Micro Chemical Systems) implemented into a commercial single mode synthesizer (Discover-CEM) has been used to perform the Suzuki cross-coupling reaction using the controlled localized heating of a Pd-supported catalyst. The temperature at the base of the micro-reactor was measured with an IR sensor placed in the bottom of the cavity. The rate conversion of the Suzuki reactions was around 50–99% with a residence time less than 60 s and a microwave power of 5–7 W. On the same basis as the previous reactor, the authors proposed in 2004 a new micro flow cell based on the principle of heating locally the catalyst. The flow cell was a U glass flow capillary reactor with an internal diameter of 800 μm, and 138 mm long, coated with a gold film at the base of the reactor to promote the microwave heating. The authors found that heat absorbed by the thin layer of gold metal increased the reaction rate and product yield knowing that the contact between the catalyst and the reactants was less than 60 s [29].

In the system described by Jachuck et al. [30], the reaction vessel is divided into two sections: a microwave transparent PTFE section where the reaction channel (270 μL) is located and an aluminum section sheltering, the cooling microchannel (600 μL). The reactor was tested for the oxidation of benzyl alcohol with flow rates of 1–5 mL/min corresponding to residence times of 3–17 s under different microwave intensities (0–39 W). An optimal condition for this reaction was determined and the authors state that this reactor has a wide rank of implications.

Single and multi-parallel capillary flow reactors were used to perform microwave organic synthesis in a commercial microwave synthesizer [31,32]. The first one was a single glass capillary tube attached to a stainless steel mixing chamber with three inlet ports and located into the commercial single-mode microwave cavity (Biotage Smith Creator Synthesizer). A set of capillary tubes was used with a range of internal diameter between 200 and 1150 μm to carry out syntheses with variable flow rates of 2–40 μL/min to obtain the residence time needed for reaction. Cross coupling and ring-closing metathesis with metal catalysts, nucleophilic aromatic substitution and heterogeneous Wittig reactions were carried out. It was pointed that the conversion rate was dependent of many parameters, such as flow rate, the internal diameter of the capillary, the power level, etc. On the concept of numbering up, a flow multi-reactor system composed of four capillary tubes was set

out to implement parallel reactions at a milligram scale based on the previous developed reactor.

3.2.2. Straight milli reactors

In order to operate at high temperatures, a backpressure system has been introduced into a microwave continuous flow tubular reactor in order so as to conduct high temperature/pressure reactions with either polar or not polar reaction mixtures [33,34]. The system consists in a cylindrical tube (1.75 mm i.d and 17 cm length) positioned vertically at the end of the waveguide of a modified Biotage Initiator Synthesizer. The reactor volume in the hot zone is 103.4 μL and is operating at high temperature/pressure up to at least 73 bar and 450 °C with flow rates up to 1 mL/min. The efficiency of the reactor was evaluated by using two reactions with high transition-state barriers (Claisen rearrangement and benzimidazole synthesis).

When the load to be heated is strongly absorbent of microwaves, it becomes difficult to control the heating, especially knowing that the permittivity varies during the course of the reaction. One way to overcome this problem consists in using a milli-reactor/heat exchanger [35]. The reactor was a quartz tubular reactor (3 mm i.d) put in a shell (7 mm i.d) where a coolant flow (toluene) to avoid the overheating of the reaction mixture. The dimensions of the reactor were defined after a study based on simulations performed with COMSOL Multiphysics. In a second step, the simulation of the electromagnetic field and the liquid circulation was done showing that the temperature profiles in the reactor are highly depending on the velocity of the liquid especially on millimeter sizes reactors. Besides a buoyancy effect due to the horizontal position of the reactor, stagnant layers were formed at the reactor walls because the flow in the reactor was rather laminar [36].

A tube made of quartz with a variable inner diameter (4–11 mm) put vertically in a single-mode cavity (SAIREM) was used as reactor at flow rates between 15 and 100 mL/min. The microwave energy absorbed was calculated by an indirect manner by a heat balance on the reactor assuming heat loss is done by natural convection. The heating efficiency increased linearly with the load diameter reaching a maximum of 78% and was restricted by the propagation diameter. The temperature does not increase uniformly throughout the axial direction of the load suggesting the presence of non-uniform electromagnetic field intensity [28].

The placement of several microwave single-mode cavities serially connected all, to only one generator has been also investigated for scale-up the microwave continuous flow synthesis in a single-mode cavity [37].

Operating at elevated pressures up to 100 bar, a reaction vessel – a cylindrical quartz tube (1.5 mm i.d, 100 mm length) was introduced into a cylindrical single-mode cavity (TM10) [38]. The temperature recorded using a radiation thermometer is monitored by a resonance frequency auto-tracking function. The reactor was successfully tested with a continuous synthesis of copper nanoparticles, operating at elevated temperature and pressure increases the reaction rate thereby enhance production scale.

To perform heterogeneous reactions, the synthesis of CuInSe2 nanocrystals, a tubular microwave segmented flow reactor (PTFE tube of 1.59 mm i.d) was implemented into a single mode cavity, connected to peristaltic pumps through a T-mixer [39]. To prevent the deposition of nanocrystals on the wall of the reactor hence the risk of sparking, a stream of segmented gas-liquid allows better mixing of the heteregeneous medium. The use of microwave heating combined with flow technology resulted into the synthesis of high quality nanoparticles in a short time and at a lower cost.

To increase the electric field density and to get an homogeneous temperature within a microwave continuous flow reactor, a particular riged waveguide optimized was developed [40]. The system consists in an axial ridged waveguide (a ridge of 4 mm i.d) with a TE_{10} mode where one to several vertical PTFE tubes with different internal diameters were put trought it. COMSOL Multiphysics was used as a simulation tool to calculate the electric field distribution. The authors then selected two models of the reactors implementation as being the most efficient for a temperature between 0 and 40 °C.

3.2.3. Coil millireactors

The coil reactor was designed to make the best use of the cavity small space and maximize the reaction time by increasing the reactor length.

A set of 26 reactions performed in a microwave continuous flow system composed of a quartz or Teflon coil (a tubing of 3 mm i.d, and 3 m in length) placed in a microwave oven was reported as one of the first implementation of microwave continuous flow [41,42]. A simple concept that operates at 200 °C, under a pressure of 140 bar, with a flow rate of 15 mL/min and offers a residence time of 1–2 min. In the same way, early in 1990, Chen et al. [43,44] reported a microwave continuous flow system to carry out safely chemical reactions on a scale higher than 20 g. The reaction vessel was a Teflon coil of about 10 mL placed in a modified commercial microwave multimode oven and fed with an HPLC standard pump. Five reactions (esterification, racemization, hydrolysis, substitution and cyclization) were successfully carried out at more than 20 g scale in this reactor.

An isothermal continuous flow reactor, 20 mm diameter coil made of quartz (3 mm i.d) enveloped with a PTFE heat exchanger inserted in a single mode cavity was presented by Matsuzawa et al. [45]. Fiber-optic probes were used to record the temperature at different points of the reactor. To optimize the design of the reactor and the applicator for a better efficiency, experiments and simulations were performed to determine the influence of the materials forming the reactor and the velocity of the liquids on the temperature. The Suzuki-Miyaura coupling synthesis was used to evaluate the reactor performances.

A flow cell coil was also used in order to safely scale up certain chemical reactions to multigram quantities in a commercial single-mode cavity (Emrys Synthesizer) [46]. It consists of a borosilicate glass protective wrap (100 mm × 10 mm) containing a borosilicate glass coil (i.d. 3 mm) with a total volume of 4 mL. A variety of reactions at flow rates between 0.25–1 mL/min were successfully scaled up to equal or higher yields when compared with those obtained under conventional heating (aromatic nucleophilic substitution, esterification, and the Suzuki cross-coupling).

4. Characterization of microwaves continuous-flow systems

4.1. Temperature measurement, power measurement, electromagnetic field

The knowledge of the temperature is a key data, which is essential in any process under microwave first because it allows maintaining a constant temperature inside the system by regulating of the incident power of the MW generator. In chemical flow synthesis, temperature becomes a control parameter of the process and the choice of its location into the system is crucial. Temperature measurement can be carried out into the system by implementing some specific sensors. It has been shown in previous work that internal sensors such as optical fibers are preferred to external system such as infrared probe [47] because they give a value of the medium temperature instead of a wall temperature. Note that in the literature, many enhancements in chemical reactions have been reported as a microwave effect, which, in reality, were only due to a wrong temperature measurement.

Fig. 4. A bolometer to measure indirectly the absorbed microwave power.

The measurement of the absorbed power is also a crucial parameter which could be realized indirectly by implementing bolometers (see Fig. 4). From energy efficiency, generally systems run correctly when a minimum of 75% of the incident power is absorbed.

Local temperature and power can be easily measured but some essential information like the electromagnetic field distribution cannot be obtained experimentally. The calculation of the electromagnetic field distribution inside the channel provides information about the energy distribution and the temperature profile. They could be determined using commercial numerical codes such as COMSOL, Quickwave, ANSYS . . . They are all based on the resolution of Maxwell's equations. The input data include the electromagnetic properties and the physical properties of the fluid and their variation with temperature, the dimensions of the microwave cavity and the incident power.

Electromagnetic field patterns are useful to analyse how the energy is dissipated into the material, and allows to verify if the sample to heat is located correctly into the cavity, at a position where the electric field reach its maximum (Fig. 5). Information about the absorbed power is also available.

Fig. 6 shows how a temperature sensor (here an optic fiber introduced in a glass steel sleeve) can interact and modify the temperature profile into the reactor even if the sensor is not much sensible to the microwaves. Recently, this effect was also described in [36] showing that any inside element could disturb the temperature distribution by disturbing the flow pattern.

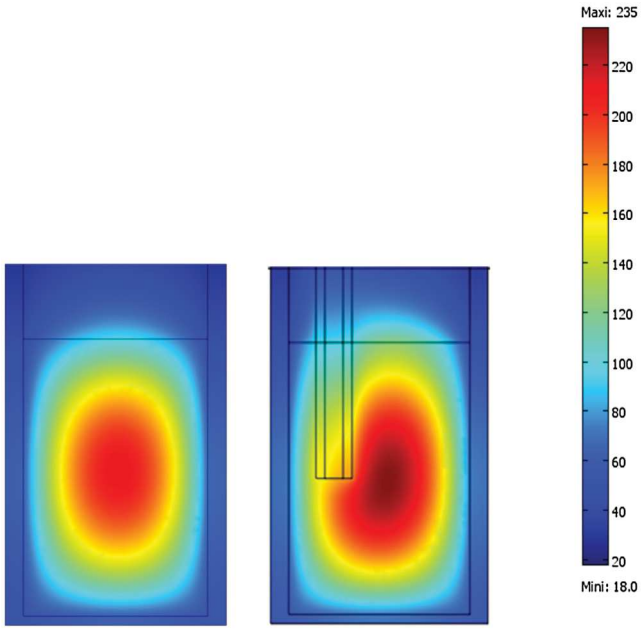


Fig. 6. Modification of the temperature profile by the implementation of a temperature sensor [48].

4.2. Hydrodynamic characterization

4.2.1. Flow regime and mixing

The flow regime and the mixing are two main points to be considered in order to increase the performances in terms of reaction rate, conversion and selectivity and to get more reproducibility between the reactions. The flow regime developed into the channel could be laminar or turbulent depending essentially on the flow rate as the operating parameter. For Reynolds numbers inferior to 2300, the flow regime is laminar and the velocity profile into the channel becomes parabolic when the flow is fully developed which is not very suitable to get good mixing (Fig. 7). This could be improved by using channels with special geometries where the disturbances created into the liquid flow enhance the radial movement. Fig. 7 shows the influence of the channel shape on the hydrodynamics; compared to a straight channel, the streamlines in a corrugated channel are not parallel to

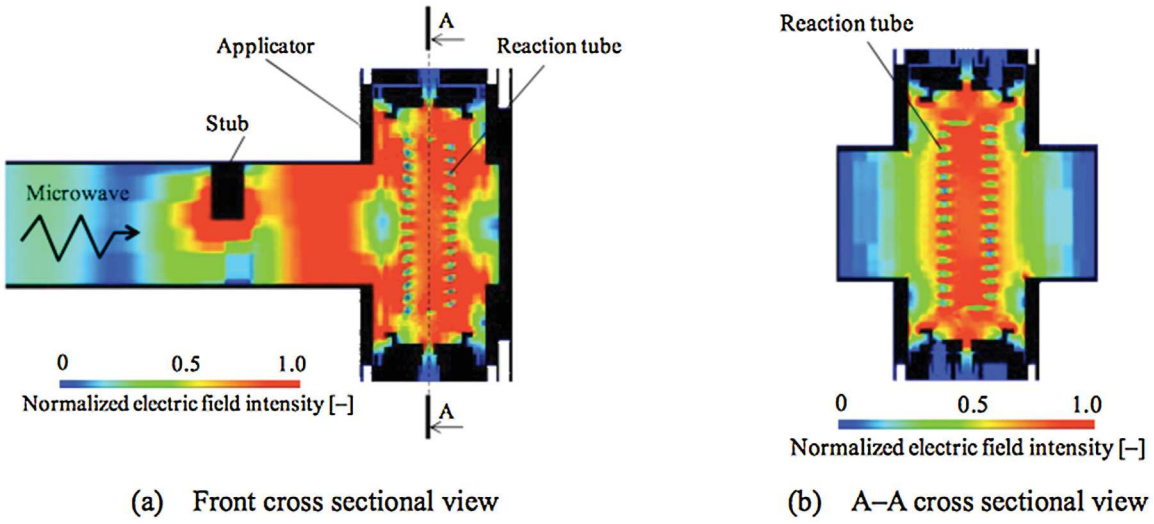


Fig. 5. Simulation of the electric field intensity in the waveguide [45].

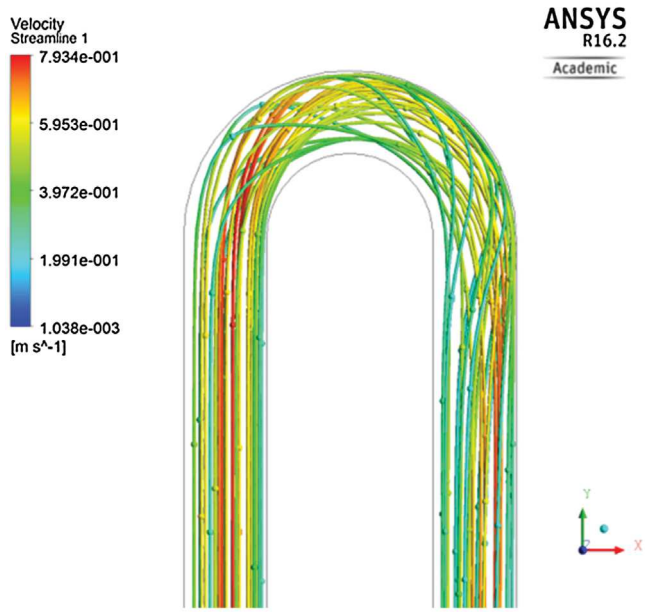


Fig. 7. Streamlines in a curved reactor (Ansys-CFX) at Re: 194.

the flow axis at the bend level. The streamlines cross over each other, indicating the fluid particles are being mixed in the tangential direction and a significant secondary flow is formed, which is able to provide mixing compared with a flow in a straight channel. This secondary flow called Dean vortices is due to the centrifugal force encountered at the bend and to the pressure gradient which generate counter-rotating vortices in the channel cross-section (Fig. 8).

Mixing could be also improved by using microstructured channels with special internal striations [49].

Turbulence could also promote mixing when Re numbers are higher than 10^4. Many studies based on experimental measurement by Laser techniques and on CDF simulations report on the design of the channels and their impact on flow field [50].

In continuous-flow microwave systems, the length of the tubular reactor is generally fixed and the flow rate is often adapted according to the kinetics of the reaction. A compromise between the velocity (i.e. flow rate) and the time residence has to be found. The geometry of the channel is generally very simple and often reduced to a simple tube. It is obvious that better reaction rates and conversion could be obtained if hydrodynamics is re-examined.

4.2.2. Pressure drop

The pressure of a liquid flowing into a channel decreases due to friction between the interior walls of the channel and the moving fluid. An understanding of the pressure loss is essential in continuous flow reactors; it depends on the fluid velocity, the fluid characteristics and the geometry of the channel. The calculation of the pressure drop ΔP (Pa) involves the Fanning friction factor, f (−), which represents the ratio between the local shear stress and the local flow kinetic energy density and which is function of the roughness of the channel and the level of turbulence within the liquid flow (Reynolds number). The pressure drop can be calculated by:

$$\Delta P = 2f\rho u^2 \frac{L}{Re_h}$$

where $Re_h = \frac{\rho u d_h}{\mu}$, Reynolds number (−)

with u the fluid velocity ($m\,s^{-1}$); L the channel length (m); ρ the fluid density ($kg\,m^{-3}$); d_h the hydraulic diameter (m); μ the fluid dynamic viscosity (Pa s)

The Fanning factor is depending also on the geometry of the channels. It is well known that for a cylindrical channel, its value is 16/Re in laminar flow. Moreau et al. [51] have reported some values of the Fanning factor for different milli-structured reactors.

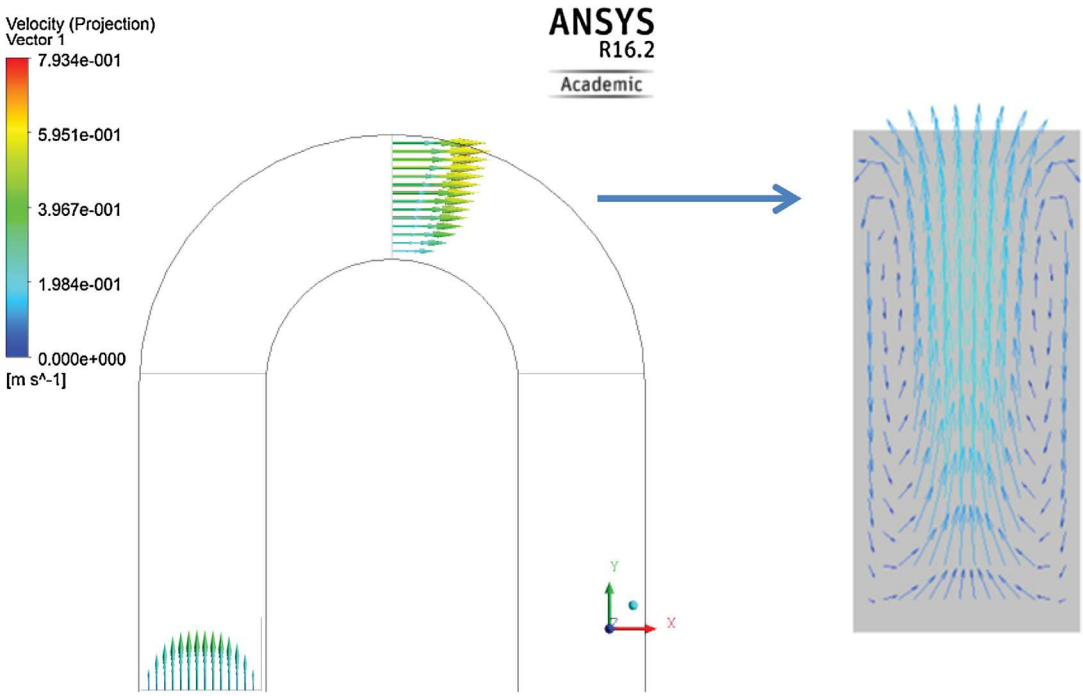


Fig. 8. (left) Axial velocity profile in the straight region and in the middle of the bend in a reactor at Re: 194–(right) velocity field for the cross section at the middle of the bend with recirculation loops at Re: 194.

4.2.3. Residence time distribution

The residence time distribution RTD is a probability distribution function that describes the time that the fluid elements spend into the reactor, thus giving information on hydrodynamics in particular on the axial dispersion and macromixing that allows the characterization of the reactor at a global level. The Peclet number ($Pe = uL/D_{ax}$ with u the fluid velocity ($m\,s^{-1}$); L the length of the channel (m); D_{ax} the diffusion coefficient ($m^2\,s^{-1}$)) helps to determine if the reactor behaviour is close to a perfect stirred tank or a plug flow reactor. In a plug flow reactor obtained when $Pe > 100$, each element of fluid has the same residence time and the stagnant zones are avoided, that could be a key factor on the selectivity of chemical reactions. The coefficient of the axial dispersion is obtained by the deconvolution of the DTS curve [52]. This graph reports the detection of a tracer at the exit of the reactor; on Fig. 9, the peak does not exhibit some tails that indicate the absence of dead zones.

4.3. Coupling hydrodynamics and electromagnetic field simulation

Numerical modelling of continuous flow microwave heating includes coupling of three physics phenomena (electromagnetism, fluid flow and heat transfer), which can be realized by solving the following governing equations: Maxwell's equations, Fourier's energy balance and Navier-Stokes equation. This new approach to design and to optimize the continuous flow microwaves reactors is not easy to implement and it requires a large knowledge in many scientific fields, first to select the relevant input data and then to analyse correctly the results. Most of the commercial RF codes propose useful modules to take in consideration all the coupled phenomena and they have been used in most of cases for modelling MW batch systems [53]. Studies involving continuous flow are more recent [54] and there are still limited.

One approach consists in replacing the Maxwell's equation by Lambert's law which is less expensive in terms of calculation time [55]. It is recommended when the volume of the object is large and reasonable results are obtained.

Using a 3D modelling of a tubular milli reactor-heat exchanger, it has been shown that an important temperature gradient into the channel could exist which is specially developed into the stagnant zones [36]. The presence of internals and the influence of the fluid velocity on the temperature profiles have been studied putting in hand the importance of the hydrodynamics on the heating process which prevails ahead of the microwave energy dissipation.

Recently, Salvi et al. [56] proposed a 3-D simulation of the continuous flow heating of Newtonian and non-Newtonian liquids using different models available into COMSOL. Provide the use of a correctly refined mesh, they show the good prediction of the model in terms of absorbed power as well as for the temperature.

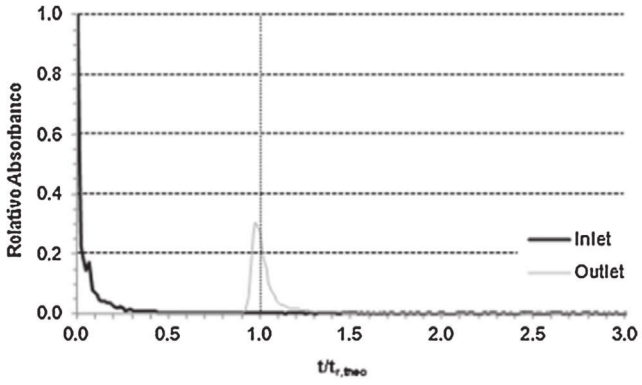


Fig. 9. RTD curve in a corrugated channel reactor at Re: 2056 (from [52]).

5. Conclusions

The main advantages for microwaves are related to a rapid increase of the bulk temperature (10 K/s), no high temperature at the vessel wall. Sometimes a more or less selective heating of the reactants is indicated. Many other advantages have been listed previously but one question still remains, "why so few implementations in industry"? As pointed out before, one must be careful with the equipment used. With the numerous examples of the literature, it is difficult to rationalize the results, to be sure to get a good homogeneity in electromagnetic field and in temperature. In the most of cases, the design of the reactor seems to be completely ignored. This is completely unrealistic when we know how the hydrodynamics could modify the reaction rate.

A preliminary modeling is essential in combining the different existing phenomena. Determining kinetics, hydrodynamics, physicochemical parameters and especially dielectric properties is crucial. The global modeling must take into account the different components which are the reactor, the chemical medium and the microwave applicator. When the final design is achieved, the control of the process takes place. An accurate temperature measurement and power control are needed to proceed under controlled conditions. Inline power measurements are very rare, many equipment only gives a value of the input power and sometimes a global value of the reflected power. A directional coupler allows separate metering of forward and reverse power, when it is equipped with two bolometer detectors it gives an accurate measure of the power. With the latter sensor, energy optimization and fine tuning are possible. This is a key point for the economic aspects and industrial developments, because safety and energy saving play an important role.

For novel technologies, the costs related to the equipment purchase include research, tuning and adaptation. They are generally higher than equipment costs for traditional process. An economic benefit is possible on operating costs when some improvements are performed. For example, increased reaction rate, product selectivity and synthesis yield, improvement of safety, of parameters of residence time control.

In the very interesting study of Benaskar et al. [57], two actual chemical production lines were considered, 2-acetoxybenzoic acid as aspirin and 4-phenoxypyridine as antibiotic precursor in Vancocin production. The most relevant general message from this paper is that the process-design needs, in a holistic manner, have to be taken into account rather than focusing only on the reaction.

Higher energy efficiencies could be attained using single-mode microwave irradiation; however, at the moment, the energy contribution to the overall cost was found to be negligible. The impact of an integrated microwave heating and microprocessing system on profitability was demonstrated with respect to operational cost and chemical productivity. Other applicator concepts, like internal transmission line [58] or traveling wave [59] are under investigation in batch processes, applications will certainly follow to continuous reactors.

Future developments should include the expertise of complementary scientific fields. Of course chemistry remains at the heart of the problem, modelling, measurements of properties, hydrodynamics, process control and chemical engineering in general are now essential to go further towards the industrial stage.

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